

Iminopyridine Manganese and Nickel Complexes: Synthesis, Characterization and Behavior in the Polymerization of 1,3-Butadiene

Giovanni Ricci^{a*}, Benedetta Palucci^a, Simona Losio^a, Anna Sommazzi^b, Francesco Masi^c, Guido Pampaloni^d, and Massimo Guelfi^{e,f}

^a CNR-Istituto di Scienze e Tecnologie "Chimiche" "Giulio Natta" (SCITEC), Via A. Corti 12, I-20133 Milano, Italy

^b Scientific Advisor, Viale Giovanni XXIII 34, I-28100 Novara, Italy

^c Scientific Advisor, Via Galvani 7, I-26866 Sant'Angelo Lodigiano (LO), Italy

^d Scientific Advisor, Via E. Fiumalbi 29, I-56025 Pontedera (PI), Italy

^e Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, I-56124 Pisa, Italy

^f Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (C.I.S.U.P.), Università di Pisa, I-56124 Pisa, Italy



Electronic Supplementary Information

Abstract Some novel manganese and nickel complexes were synthesized by reacting manganese(II) dichloride and nickel(II) dichloride with pyridyl-imine ligands differing in the nature of the substituents at the imino nitrogen atom. All the complexes were characterized by analytical and infrared data: for some of them single crystals were obtained, and their molecular structure was determined by X-ray diffraction. The complexes were used in association with methylaluminoxane (MAO) for the polymerization of 1,3-butadiene obtaining active and selective catalysts giving predominantly 1,2 polybutadiene in case of manganese catalysts and exclusively *cis*-1,4 polybutadiene in case of nickel catalysts.

Keywords Manganese; Nickel; Catalysts; Polymerization; Polybutadiene; X-ray structures

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INTRODUCTION

The stereospecific polymerization of conjugated dienes^[1] in recent years has significantly focused on the use of catalytic systems based on transition metals and lanthanide organometallic complexes with various types of ligands having P and/or N and/or O as donor atoms (e.g., phosphines, imino-pyridines, ketoimines), with a well-defined structure.^[2,3] The reason for this trend lies in the fact that the presence of ligands on the metal atom is able, as widely expected on the basis of the polymerization mechanism of conjugated dienes,^[4] to exert a strong influence on the catalytic selectivity: polymers with different structures (*cis*-1,4; *trans*-1,4; 1,2; 3,4, iso- and syndiotactic), amorphous or crystalline, can be obtained from the various 1,3-dienes by varying the nature of the ligand on the metal atom. The use of ligands has also made it possible to obtain extremely active catalytic systems, and in particular it has been possible to obtain interesting catalytic systems even from metals that had been scarcely or even not considered in the field of stereospecific polymerization of conjugated dienes until now. This is the case of iron,^[5–12] little considered until a few years ago, and of

copper,^[13,14] on which nothing had been reported until now in the field of stereospecific polymerization of vinyl monomers, whose pyridylimine complexes, in combination with MAO, have provided extremely active and selective catalysts for the polymerization of butadiene, isoprene and myrcene, providing also rather unusual polymeric structures as regards the polymerization of conjugated dienes.

Continuing along this path, we took into consideration other metals such as manganese and nickel. To the best of our knowledge, practically nothing has ever been reported on manganese-based catalysts in the field of stereospecific polymerization, with the exception of just one paper from 1971^[15] concerning the polymerization of butadiene with the system obtained by combining MnCl₂ with AlEt₃, a catalyst characterized by very low activity and selectivity; a fair number of studies have instead been reported in the literature on the polymerization of butadiene with nickel-based catalysts,^[16–29] all of them providing polybutadienes with an essentially *cis*-1,4 structure regardless of the nature of the ligand coordinated to the nickel atom, but still having features very distant from the highly active industrial-scale catalyst (i.e., nickel naphthenate-BF₃·Et₂O-AlR₃-H₂O catalyst) as regards catalytic activity and molecular weight of the obtainable polymers.

We therefore synthesized and characterized some manganese and nickel complexes (Fig. 1) with pyridylimine lig-

* Corresponding author, E-mail: giovanni.ricci@scitec.cnr.it

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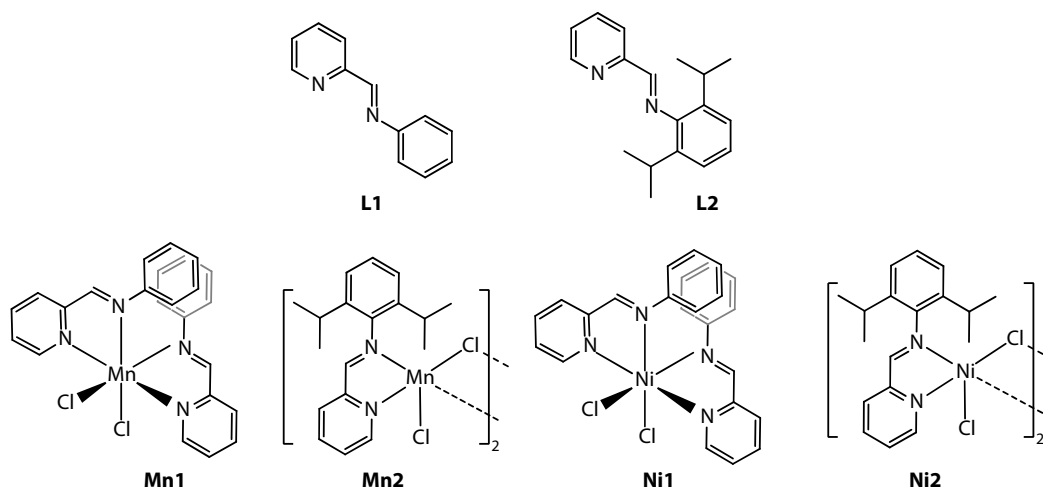


Fig. 1 Ligands and Manganese (II) and Nickel (II) complexes used in this work.

ands which had provided so much satisfaction in the case of iron and copper, and we went on to examine their behavior in the polymerization of butadiene.

Rather interesting and promising results were obtained, and in this article, we report on these preliminary findings.

EXPERIMENTAL

General Considerations

Anhydrous manganese dichloride and nickel dichloride hexahydrate (Merck, 99.9% pure) were used as received. Aniline (Merck, 99%) and 2,6-diisopropylaniline (Merck, 97%) were distilled at reduced pressure and stored in an inert atmosphere. 2-Pyridinecarboxaldehyde (Merck, 99%) and methanol (Merck, 99.8%) were used as received. Ethyl alcohol (Merck, 96% pure) was degassed under vacuum, then by bubbling dry nitrogen and kept over molecular sieves; pentane (Merck, 99% pure) was refluxed over Na/K alloy for *ca.* 8 h, then distilled and stored over molecular sieves under dry nitrogen; toluene (Merck, 99.8% pure) was refluxed over Na for 8 h, then distilled and stored over molecular sieves under dry nitrogen; dichloromethane (Merck, $\geq 98.8\%$) was refluxed over calcium hydride for 8 h, then distilled and stored over molecular sieve under dry nitrogen; diethylether (Merck, ≥ 98.7) was refluxed over Na/K alloy for *ca.* 8 h, then distilled and stored over molecular sieves under dry nitrogen. 1,3-Butadiene (Merck, $\geq 99\%$) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to -20 °C. MAO (Aldrich, 10 wt% solution in toluene), and deuterated solvent for NMR measurements ($C_2D_2Cl_4$, CD_2Cl_2 , $CDCl_3$) (Merck, $>99.5\%$ atom D) were used as received.

Synthesis of Pyridyl-imine Ligands and Pyridyl-imine Manganese and Nickel Complexes

Synthesis of ligand *N*-(pyridin-2-ylmethylene)aniline (L1)

In a 500 mL flask, 2-pyridinecarboxaldehyde (30 g, 280 mmol) and some drops of formic acid were added to a solution of aniline (26.1 g, 280 mmol) in methanol (250 mL): the mixture obtained was maintained, under stirring, at room temperature, for 48 h. Subsequently, the solvent was removed through vacuum

evaporation and the residue obtained was purified through elution on a silica gel chromatography column [eluent: mixture of heptane/ethyl acetate in ratio of 99/1 (V/V)], obtaining 38 g of a pale-yellow solid (yield=74.5%) corresponding molecular weight (MW): 182.22. Elementary analysis [found (Calcd. for $C_{12}H_{10}N_2$): C: 80.00% (79.10%); H: 5.83% (5.53%); N: 15.71% (15.37%)]. 1H -NMR ($CDCl_3$, δ , ppm): 8.70 (m, 1H, HPy), 8.41 (m, 1H, HPy), 8.80 (tds, 1H CH=N), 8.19 (d, 1H, HPy), 7.77 (dt, 1H, HPy), 7.23–7.42 (m, 1H, HPy; m, 5H, Ar).

Synthesis of ligand 2,6-Diisopropyl-*N*-(pyridin-2-ylmethylene)aniline (L2)

In a 500 mL flask, 2-pyridinecarboxaldehyde (16.86 g; 157.5 mmol) were added to a solution of 2,6-diisopropylaniline (27.93 g; 157.5 mmol) in anhydrous ethanol (250 mL): the mixture obtained was heated under reflux, for 3 h. Subsequently, the mixture was dried under vacuum to obtain a yellow oil, to which 30 mL of pentane was added. The mixture was then refrigerated for 48 h, leading to the formation of yellow crystals, which were recovered by filtration and drying under vacuum, yielding 41.7 g of a yellow crystalline powder (yield 99%). Molecular weight (MW): 266.38. Elementary analysis [found (Calcd. for $C_{18}H_{22}N_2$): C: 81.31% (81.16%); H: 8.21% (8.32%); N: 9.96% (10.52%)]. 1H -NMR (CD_2Cl_2 , δ , ppm): 8.72 (d, 1H, PyH), 8.32 (s, 1H CH=N), 8.27 (d, 1H PyH), 7.86 (t, 1H PyH), 7.39 (m, 1H PyH), 7.11–7.20 (m, 3H ArH), 3.00 (sept, 2H $CHMe_2$), 1.18 (d, 12H $C(CH_3)_2$). FTIR (nujol) (cm^{-1}): 1651 ($\nu_{C=N}$).

$Mn(L1)_2Cl_2$ (Mn1)

To a solution of manganese chloride (0.242 g, 1.92 mmol) in THF (15 mL) was added L1 (0.701 g, 3.85 mmol) and the resulting solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the resulting yellow solid was washed with two portion of diethyl ether and dried in vacuo affording 0.890 g (94.5 % yield) of $Mn(C_{12}H_{10}N_2)_2Cl_2$ as yellow powder. Elemental analysis (%): Calcd. for $C_{24}H_{20}Cl_2MnN_4$: C, 58.79; H, 4.11; N, 11.43. Found: C, 58.53; H, 4.45; N, 11.38. Selected IR data (solid state, cm^{-1}), 3066 m, 1629 m, 1594 s, 1488 m, 1441 m, 784 s.

$[Mn(L2)Cl_2]_2$ (Mn2)

To a solution of manganese chloride (0.190 g, 1.51 mmol) in THF (10 mL) was added L2 (0.402 g, 1.51 mmol) and the resulting so-

lution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the resulting yellow solid was washed with two portion of diethyl ether and dried in vacuo affording 0.536 g (90.5 % yield) of $\text{Mn}(\text{C}_{18}\text{H}_{22}\text{N}_2)\text{Cl}_2$ as light yellow powder. Elemental analysis (%): Calcd. for $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{MnN}_2$: C, 55.12; H, 5.65; N, 7.14. Found: C, 54.87; H, 5.85; N, 6.99. Selected IR data (solid state, cm^{-1}), 3065 w, 2966 s, 1632 m, 1595 s, 1445 m, 777 s.

$\text{Ni}(\text{L}1)_2\text{Cl}_2$ (**Ni1**)

To a solution of nickel chloride hexahydrate (0.200 g, 0.84 mmol) in ethanol (10 mL) was added **L1** (0.306 g, 1.68 mmol) and the resulting solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the resulting yellow solid was washed with two portion of diethyl ether and dried in vacuo affording 0.240 g (92.7% yield) of $\text{Ni}(\text{C}_{12}\text{H}_{10}\text{N}_2)_2\text{Cl}_2$ as yellow powder. Elemental analysis (%): Calcd. for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NiN}_4$: C, 58.35; H, 4.08; N, 11.34. Found: C, 58.23; H, 4.43; N, 10.34. Selected IR data (solid state, cm^{-1}), 1630 m, 1597 s, 1488 m, 778 s.

X-ray Structure Determination

Yellow single crystals of (**Ni1**) and (**Mn1**) were grown by slow diffusion of hexane or acetone, respectively, in an ethanolic solution of (**Ni1**) and (**Mn1**) at -20°C . Data collection was performed at 100 K on a Bruker D8 VENTURE diffractometer equipped with PHOTON III photon counting detector and a monochromatized MoKa ($\lambda=0.71073\text{ \AA}$) radiation, operating in Phi-Omega scan mode. Unit cell was initially refined, using APEX4.^[30] Successively, data were integrated and reduced using SAINT^[31] and XPREP.^[32] Absorption effects were corrected using SADABS.^[33] The structure was solved and refined with the aid of SHELXL-2019/1 program packages.^[34]

General Polymerization Procedure

A typical polymerization of 1,3-butadiene was carried out in a 25 mL round-bottom Schlenk flask. Prior to starting polymerization, the reactor was heated to 110°C under vacuum for 1 h and backfilled with dinitrogen. 1,3-Butadiene was condensed into the Schlenk flask kept at -20°C , then toluene was added, and the solution was brought to the desired polymerization temperature. MAO and a toluene solution (2 mg/mL) of the manganese or nickel complex were then added in that order. Polymerization was stopped with methanol containing a small amount of hydrochloric acid. The polymer obtained was then coagulated by adding 40 mL of methanol solution containing 4% of Irganox[®] 1076 antioxidant and HCl, repeatedly washed with fresh methanol and finally dried in vacuum at room temperature to constant weight.

Polymer Characterization

Attenuated total reflectance (ATR)-Fourier transform infrared spectroscopy (FTIR) spectra were recorded at room temperature in the $4000\text{--}600\text{ cm}^{-1}$ range with a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum Two spectrometer. NMR spectra were recorded on a Bruker NMR advance 400 Spectrometer operating at 400 MHz (^1H) and 100.58 MHz (^{13}C) working in the PFT mode at 103°C . NMR samples were prepared dissolving from 60 mg to 80 mg of polymer in about 3 mL of $\text{C}_2\text{D}_2\text{Cl}_4$ in 10 mm probes and referred to hexamethyldisilane (HMDS), as internal standard. The relaxation delay was 16 s. The molecular weight average (M_w) and the molecular weight distribution (M_w/M_n)

were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system equipped with a refractometer detector. The experimental conditions consisted of three PL Gel Olexis columns, ortho-dichlorobenzene as the mobile phase, 0.8 mL/min flow rate, and 145°C temperature. The calibration of the SEC system was constructed using eighteen narrow M_w/M_n PS standards with molar weights ranging from 162 g/mol to 5.6×10^6 g/mol. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of DCB with 0.05% of BHT as antioxidant. Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid nitrogen subambient device. The sample, ca. 4 mg, was placed in a sealed aluminum pan, and the measurements were carried out using heating and cooling rates of $20^\circ\text{C}/\text{min}$. The microstructure of the resultant polymers [*i.e.*, *cis*-1,4 unit content (%) and 1,2 unit content (%); syndiotactic index (*rrrr*%) of the 1,2 poly(1,3-butadiene)s] was determined by ^1H - and ^{13}C -NMR spectra, according to the literatures.^[35,36]

RESULTS AND DISCUSSION

Synthesis and Characterization of Manganese and Nickel Complexes

The nickel complexes were synthesized according to slight modifications of the procedures reported in the literature,^[37–39] starting from $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and ligands **L1** and **L2**, in ethanol at room temperature. For the **Ni1** complex, at variance to the literature,^[37] a bis-chelate compound was obtained even when using a $\text{Ni}/\text{L1}$ molar ratio = 1. Otherwise, with **L2**, a dinuclear chlorine-bridged compound was formed, probably due to the increased steric hindrance of the two isopropyl groups on the benzene ring in this ligand. The manganese complexes $\text{Mn}(\text{L}1)_2\text{Cl}_2$ and $[\text{Mn}(\text{L}2)\text{Cl}_2]_2$, **Mn1** and **Mn2** respectively, were synthesized according to the procedure reported in the literature, *i.e.*, by reaction of MnCl_2 with **L1** and **L2** at room temperature.^[40] Attempts to obtain the $\text{Mn}(\text{L}1)\text{Cl}_2$ compound were unsuccessful.

Single crystal X-ray diffraction studies

The crystallographic data obtained for (**Ni1**) and (**Mn1**) complexes, are summarized in Table 1 and the important bond lengths and bond angles are listed in Tables 2 and 3. The complex (**Ni1**) crystallizes in a tetragonal space group $P4_12_12$, with $Z=4$ for the formula unit $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NiN}_4$. A view of the molecular structure is reported in Fig. 2. The Ni(II) center has a distorted octahedral geometry, as indicated by the $\text{N}1\text{--Ni}1\text{--N}1\#1$ ($168.8(2)^\circ$) and $\text{N}1\text{--Ni}1\text{--Cl}1$ ($170.36(11)^\circ$) bond angles. The pyridyl rings are located on opposite site of the octahedral plane and each of the imino nitrogens are opposite of the chlorine atoms. In the structure the $\text{Ni}\text{--N}(\text{Imino})$ ($2.069(4)^\circ$) bond distance is shorter than the $\text{Ni}\text{--N}(\text{pyridyl})$ ($2.140(4)^\circ$) bond distance and the two lengths are within the range of the Nickel complex with the **L2** ligand reported in literature.^[37–39] The perspective view of the compound (**Ni1**) in Fig. S1 (in the electronic supplementary information, ESI) shows an interesting intramolecular interaction that involves the chlorine atom (Cl1) and the hydrogen (H12) with a length $\text{H}12\cdots\text{Cl}1$ of 2.783 Å. Fig. S2 (in ESI) shows a further π -stacking interaction between the two pyridyl rings of two different units inside the unit cell with a distance in the range of 3.224–3.283 Å.

Table 1 Crystal data and structure refinement details of (Ni1) and (Mn1).

CCDC ID	2358922	2358921
Molecular formula	C ₂₄ H ₂₀ Cl ₂ N ₄ Ni	C ₁₂ H ₁₀ ClMn _{0.5} N ₂
Molecular weight (g·mol ⁻¹)	494.05	245.14
Temperature (K)	100(2) K	100(2)
Wavelength λ	0.71073 Å	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	P4 ₁ 2 ₁ 2	C2/c
a	8.6378(4) Å	24.6824(13) Å
b	8.6378(4) Å	14.8472(6) Å
c	36.980(4)	14.0895(7) Å
β	90°	118.426(2)°
V (Å ³)	2759.1(4)	4540.8(4)
Z	4	16
Calculated density (g·cm ⁻³)	1.189	1.443
Absorption coefficient (mm ⁻¹)	0.912	0.836
F(0 0 0)	1016	2008
Theta range (°)	2.42 to 25.01	2.00 to 25.04
Index range	-10 ≤ h ≤ 10, -10 ≤ k ≤ 9, -44 ≤ l ≤ 43	-29 ≤ h ≤ 29, -17 ≤ k ≤ 17, -16 ≤ l ≤ 16
	15644/2434 [R(int) = 0.1029]	40632/4022 [R(int) = 56]
Reflections measured/independent	Multi-Scan	Multi-Scan
Absorption correction	Direct methods	Direct methods
Structure solution technique	XT, Version 2018/2	XT, Version 2018/2
Structure solution program	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Refinement method	SHELXL-2019/1 (Sheldrick, 2019)	SHELXL-2019/1 (Sheldrick, 2019)
Refinement program	2434/0/141	4022/0/280
Data/restraints/parameters	1.091	1.029
Goodness of fit on F ²	R1=0.0411, wR2=0.0883	R1=0.0340, wR2=0.0694
Final R indices [I > 2σ(I)]	R1 = 0.0458, wR2 = 0.0911	R1=0.0514, wR2=0.0778
Final R indices [all data]	w = 1/[σ ² (F _o ²) + (0.0234P) ² + 2.3016P]	w = 1/[σ ² (F _o ²) + (0.0280P) ² + 8.3714P]
Weighting scheme	where P = (F _o ² + 2F _c ²)/3C	where P = (F _o ² + 2F _c ²)/3C
Largest diff. peak and hole (e·Å ⁻³)	0.289 and -0.448	0.522 and -0.279

$$R = \{\sum[w(|F_o| - |F_c|)] / \sum w(|F_o|)\}, R_w = \{\sum[w(|F_o| - |F_c|)^2] / \sum w(|F_o|^2)\}^{1/2}, wR^2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)\}^{1/2}$$

Table 2 Selected bond lengths (Å) and angles in (Ni1).

Ni1-N1(imino)	2.069(4)	N2-Ni1-N2#1	168.8(2)
Ni1-N2(pyridyl)	2.140(4)	N1-Ni1-Cl1	170.36(11)
Ni1-Cl1	2.3984(12)	N2-Ni1-N1#	93.19(15)
N1-C12(imino)	1.283(6)	N2-Ni1-N1	78.28(14)
N1-C1	1.421(6)	N1-Ni1-Cl1#1	91.85(10)
N2-C11(pyridyl)	1.344(6)	N2-Ni1-Cl1#1	92.37(11)
N2-C7(pyridyl)	1.360(6)		

Symmetry transformations used to generate equivalent atoms #1 -y+1, -x+1, -z+3/2

Table 3 Selected bond lengths (Å) and angles in (Mn1).

Mn1-N1(pyridyl)	2.249(2)	N1-Mn1-N3	151.09(7)
Mn1-N2(imino)	2.343(2)	Cl1-Mn1-N4	159.36(5)
Mn1-N3(pyridyl)	2.263(2)	N2-Mn1-Cl2	165.06(5)
Mn1-N4(imino)	2.475(2)	Cl2-Mn1-Cl1	99.64(2)
Mn1-Cl1	2.4503(7)	N3-Mn1-N2	97.83(5)
Mn1-Cl2	2.4001(7)	N2-Mn1-N4	74.91(7)
N4-C18(imino)	1.276(3)	N1-Mn1-N4	82.70(7)
N4-C19	1.426(3)	N1-Mn1-Cl1	108.27(5)
N2-C6(imino)	1.281(13)	N2-Mn1-Cl1	91.61(5)
N2-C7	1.419(3)		

The structure of complex (Mn1) was reported as toluene- or methanol solvated species^[40] in the monoclinic P2_{1/n} space group. The crystal we obtained does not contain lattice solvent and belongs to the monoclinic space group C2/c, with

Z=16 for the formula C₁₂H₁₀ClMn_{0.5}N₂, see Fig. 3. Bond lengths and angles are slightly different from those reported for the solvated species, but still within the typical range for Mn(II) complexes.^[41,42] Contacts (3.439–3.444 Å) are present

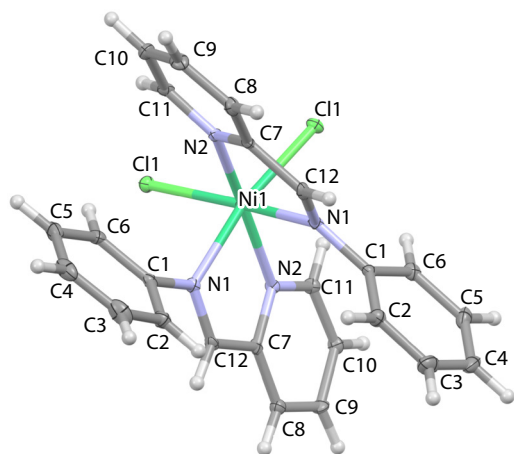


Fig. 2 Molecular structure of (**Ni1**). Displacement parameters are drawn at 30% probability level.

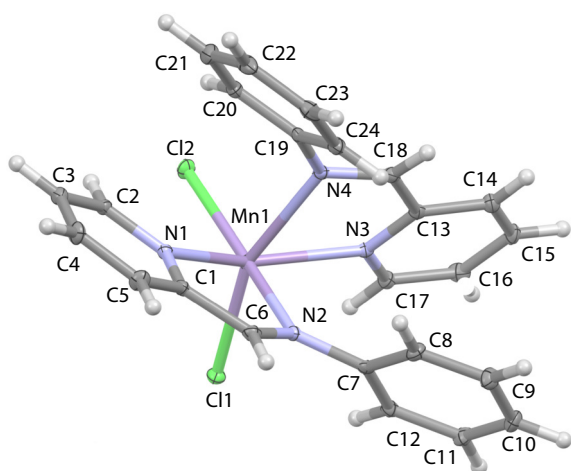


Fig. 3 Molecular structure of (**Mn1**). Displacement parameters are drawn at 30% probability level.

between Cl2 and the carbon atoms C2 and C14 of the pyridyl ring (Fig. S3 in ESI).

Polymerization of 1,3-Butadiene

In Table 4, selected results of the polymerization of 1,3-butadiene with catalysts obtained by combining the above manganese(II) and nickel(II) complexes with MAO are listed.

Catalysts based on manganese complexes provide predominantly 1,2 polybutadienes (1,2 content about 60%); the

cis-1,4 and 1,2 units are likely randomly distributed along the polymer chain, as suggested by the presence, in the olefinic zone of resonances at 125.7 and 128.8 ppm assigned to *cis*-1,4 units and at 112.4 ppm ascribed to 1,2 units isolated between 1,2 and *cis*-1,4 units respectively (see Fig. 4 and Figs. S4–S12 in ESI). Moreover, *cis*-1,4 units and 1,2 units, involved in sequences of *cis*-1,4 units (at least three units) and 1,2 units, can be observed at 127.8 and 112.3 ppm, respectively.

The polymer molecular weight is very high, up to 1.3×10^6 g/mol, and the polymer molecular weight distribution narrow, in the range of 2–5 (see Figs. S13–S15 in ESI). The catalytic activity is in general not very high and seems to slightly decrease with increasing the substitution on the phenyl ring (as already observed in case of analogous iron and copper catalysts) and largely decrease with decreasing the MAO/Mn molar ratio (*cf.* entries 1–3 and 4–5); the catalytic selectivity does not appear to be affected by the nature of the ligand and the MAO/Mn ratio. The data available are however still too few to draw definitive conclusions, and the trend observed will have to be confirmed once the polymerization behavior of other complexes with different pyridylimine ligands has been examined, especially in light of the results previously obtained with similar iron and copper-based systems.

Nickel-based catalysts invariably provide very high *cis*-1,4 polybutadiene, regardless of the nature of the ligand and the MAO/Ni ratio. These findings can be confirmed by the analysis of the FTIR spectra of selected poly(1,3-butadiene)s reported in ESI (Fig. S16 in ESI), in which the typical absorption band at 733 cm^{-1} , indicative of the presence of a *cis*-1,4 structure, is much more intense than that at 911 cm^{-1} , ascribed to 1,2 units.

Molecular weight is rather low, but this is not surprising for nickel-based systems (see Fig. S17 in ESI). The same discussion made above for manganese, relating to the synthesis and testing of different pyridyl-imine complexes, is equally valid for nickel.

The results obtained in the polymerization of 1,3-butadiene with the catalytic systems based on the manganese complexes **Mn1** and **Mn2** are quite similar to those obtained with the analogous iron based catalyst.^[9] We could therefore hypothesize in case of manganese a structure of the active catalytic center similar to that of iron, with the monomer *cis*- η^4 coordinated, the growing chain bonded to the manganese atom through an anti η^3 -allyl group, the bidentate ligand on the manganese atom, and a preferred insertion of the incoming monomer at C3 of the η^3 -allylic unit with the formation of

Table 4 Polymerization of 1,3-butadiene with Manganese and Nickel Based Catalysts^a.

Run	Mt_complex (mmol)	Al/Mt (molar ratio)	Time (h)	Yield (g)	Conv. (%)	<i>cis</i> -1,4 ^b (%)	1,2 ^b (%)	M_w^c (g/mol)	M_w/M_n^c
1		3000	5	0.77	32.9	42.3	57.7	683300	5.1
2	Mn1	1000	5	0.31	9	40.3	59.7	1241500	5.4
3		200	22	traces					
4	Mn2	1000	10	0.37	31.4	39.5	60.5	1315400	1.9
5		100	22	traces					
6	Ni1	1000	4	1.40	100	95.0	5.0	48650	8.4
7		200	4	1.06	75.7	94.8	5.2	56100	5.2
8	Ni2	1000	4	0.51	36.4	94.8	5.2	67600	3.6

^a Polymerization conditions: 1,3-butadiene, 2 mL; toluene, total volume 16 mL; MAO; Mt, 5×10^{-6} mol; ^b Determined by ¹H-NMR spectroscopy; ^c Molecular weight (M_w) and molecular weight distribution (M_w/M_n) determined by SEC chromatography.

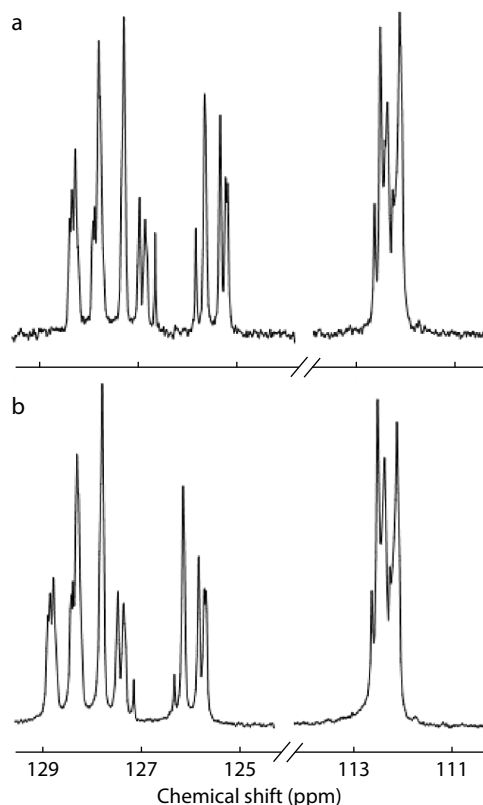


Fig. 4 ^{13}C -NMR spectra (olefinic region) of the poly(1,3-butadiene)s from manganese catalysts (Table 4, runs 2 (b) and 4 (a)).

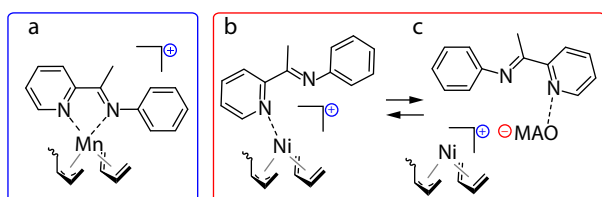


Fig. 5 Possible active site structures in case of manganese and nickel catalyst.

a 1,2 monomeric unit (Fig. 5a).

The results obtained instead in case of nickel are very similar to those obtained with the analogous cobalt-based catalysts.^[2,3] We could indeed suppose a catalytic center structure like that shown in Figs. 5(b) and 5(c): the monomer *cis*- η^4 coordinated, the growing chain bonded to the nickel atom through an anti η^3 -allyl group, the bidentate ligand coordinated to the nickel atom with only one nitrogen atom or completely displaced from the nickel atom and migrated on to MAO, and an insertion of the incoming monomer exclusively at C1 of the η^3 -allylic unit with the formation of *cis*-1,4 units.

CONCLUSIONS

Some novel manganese(II) and nickel(II) complexes bearing pyridyl-imine ligands were synthesized and fully characterized. Their behavior, in combination with MAO, was examined in the polymerization of 1,3-butadiene. They were found able to selectively polymerize 1,3-butadiene, exhibiting at the same time a

good activity. Some influence of the nature of the ligand and the MAO/Mt ratio on catalytic activity has been observed, but this effect will have to be confirmed once the polymerization behavior of other complexes with different pyridyl-imine ligands has been examined. Our idea and hope are that the use of different types of ligands can lead to greater control of catalytic selectivity, allowing to obtain more stereoregular polymers, not only from butadiene but also from other diene monomers. This is truly more than a hope, in light of the results previously obtained with the Cr, Co, V, Fe and Cu based systems, which have clearly indicated that most of the metals, once the right ligands have been identified, are able to provide active and selective catalysts for the polymerization of conjugated dienes.

Finally, it should be emphasized that to date nothing has been reported on manganese-based catalysts, and little has been investigated on nickel-based ones in the field of the stereospecific polymerization of conjugated dienes, so it seems to us useful to report on these preliminary results. Work is in progress on the synthesis of additional manganese and nickel complexes with various organic ligands and on their use, in combination with the appropriate alkylating agents, for the polymerization of 1,3-dienes.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-024-3233-2>.

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